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A Chemical Kinetic Study of Octane Sensitivity

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Abstract: Significant progress has been made in recent years on chemical kinetic factors that influence low temperature hydrocarbon fuel oxidation. We now have a much more detailed picture of such phenomena as cool flame chemistry, alkylperoxy radical isomerization reaction pathways, negative temperature coefficient behavior, and engine knock in spark-ignition (SI) engines. Some of the metrics that are used to characterize low temperature oxidation phenomena in SI engines involve octane numbers, including the two most common, Research Octane Number (RON) and Motored Octane Number (MON), which provide valuable information that are useful in fuel characterization. However, the difference between RON and MON values, which has developed the name of Octane Sensitivity, is much less understood and its value is often debated. In this paper, we use chemical kinetic modeling to explore the details that determine the Octane Sensitivity of selected hydrocarbon fuels. In particular, we focus on differences in reactivity under RON and MON test conditions to identify individual classes of elementary reactions that are most responsible for differences between the Octane Sensitivities of familiar alkane and olefin fuels, since alkanes are commonly regarded as fuels with little or no Octane Sensitivity, while many olefin fuels are observed to have large Octane Sensitivities. We are particularly interested in the role that allylic C-H bonds in olefin and biodiesel fuel molecules play in retarding low temperature fuel reactivity and in enhancing higher temperature reactivity

Keywords: *Chemical Kinetics, Autoignition, Engine Knock*

1. Introduction

Chemical kinetic simulations have grown steadily in complexity, accuracy and impact on combustion chemistry research, taking a place with chemical theory and advanced, optical diagnostics as essential tools for probing practical energy systems and understanding fuel oxidation. Recent improvements in kinetic modeling techniques, along with dramatic advances in computer capacities and speed have made it possible to model kinetics of complex fuels such as large n-alkanes [1], lightly branched alkanes [2], other large alkane fuels such as 2,2,4,4,6,8,8-heptamethyl nonane [3], and even biodiesel fuels [4]. Kinetic models and associated sensitivity analyses can identify specific chemical reactions, reaction rates, reaction pathways, bond energies and other thermochemical parameters that are particularly important and can accelerate development of models and general understanding of many practical combustion processes. Kinetic modeling is most valuable when a combination of new experiments and kinetic modeling address fundamental processes that have significant impacts on practical combustion problems.

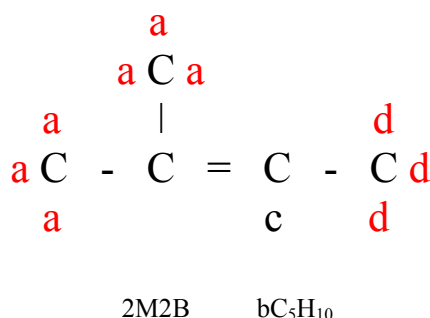
In a very recent study [5], new shock tube and stirred reactor experiments were used to build and validate a new chemical kinetic reaction mechanism for combustion of 2-methyl, 2-butene (2M2B, C_5H_{10}) over a wide range of temperatures and equivalence ratios. 2M2B was selected

for attention for a very particular reason. Due to the location of the C=C double bond in the middle of the fuel molecule, nine of its ten C-H bonds are resonantly stabilized allylic bonds, which produce allylic C₅H₉ radicals by H atom abstraction from the fuel, while the remaining C-H bond in 2M2B is a very strong vinylic bond that produces extremely small amounts of vinylic pentenyl radicals. This makes 2M2B an ideal fuel to study the kinetics of allylic hydrocarbon radicals and bonds and explore the role that C=C double bonds and their associated allylic radicals play in both idealized laboratory experiments and very practical engine applications.

Olefins are present in transportation fuels including gasoline, aviation fuel, and diesel fuel in significant amounts, as much as 15-20% of gasoline, and they contribute to determining the ignition properties of those fuels, including the Octane Numbers that measure resistance to knocking behavior in spark-ignition engines. Smaller, branched olefins such as 2M2B are well known to exhibit strong Octane Sensitivity, with fairly high Research Octane Numbers (RON) but smaller Motored Octane Numbers (MON). For example, the RON and MON for 2M2B are 97.3 and 84.7, respectively [6], and this variation persists to olefin species as large as 2,4,4-trimethyl-1-pentene (C₈H₁₆) with RON greater than 100 and MON of 86.5. Leppard [7] discussed these octane sensitivities quite thoroughly and attributes them to a lack of low temperature reactivity in these olefins, since these sensitive fuels produce little or no Negative Temperature Coefficient (NTC) behavior or low temperature reactivity. However, this explanation is a correlation and not an explanation, in fundamental terms, of why this lack of low temperature reactivity produces the low MON values observed for such fuels. Several factors have been suggested to explain this lack of low temperature reactivity, including the presence of multiple allylic radicals that are produced by olefin fuels, and the present fuel offers an excellent opportunity to examine the reactivity of allylic radicals over a wide range of reaction temperatures.

2. Background

We began our study with the kinetics of 2M2B, which can be visualized as:



where the C=C double bond is located in the middle of the fuel and the letters **a**, **c**, and **d** represent structurally equivalent H atoms. The H atoms denoted in red represent the H atoms bonded at allylic sites, while the H atom denoted by ‘c’ is located at the vinylic site. We use several naming systems for this fuel molecule, using 2M2B as well as ‘bC₅H₁₀’, which indicates that the C=C double bond is located at the central location in the molecule.

In our previous paper [5], we summarized the detailed chemical kinetic reaction mechanism developed for combustion of 2M2B. The results of extended validations of the mechanism were presented, using comparisons between computed and experimentally measured ignition delay

times in high temperature shock tube experiments, and measured chemical species mole fractions of fuel, products, and intermediate species from stirred reactor experiments. Here we show one set of results from each family of experiments to illustrate the level of agreement between experiments and the kinetic model computed results, and refer the interested reader to Ref. [5] for further details of the experiments and modeling results.

Shock tube ignition delay times were measured at Texas A&M University of 2M2B/O₂ mixtures, diluted by 99% Argon, at post-shock pressures of about 1.7, 11, and 31 bar, and fuel/O₂ equivalence ratios of 0.5, 1.0, and 2.0. One group of these results and comparisons is shown in Fig. 1, where lines show computed ignition delays and symbols are the measurements.

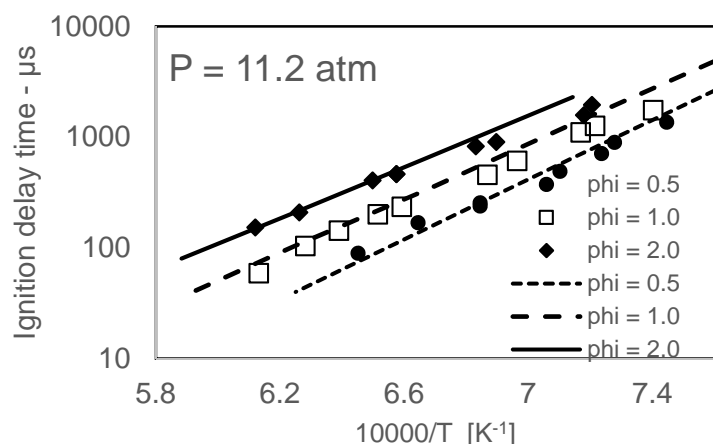


Fig. 1. Shock tube ignition delay times for 2M2B/O₂/Ar mixtures at 11.2 bar pressure. Experimental results shown as symbols, computed results shown as lines.

The stirred reactor experiments were for stoichiometric mixtures of 2M2B/O₂ at atmospheric pressure, diluted by 91.5% helium. Species concentrations of 36 different chemical species were measured, most of which were summarized and compared with computed results in Ref. [5], and representative examples of measured and computed mole fractions are shown in Fig. 2..

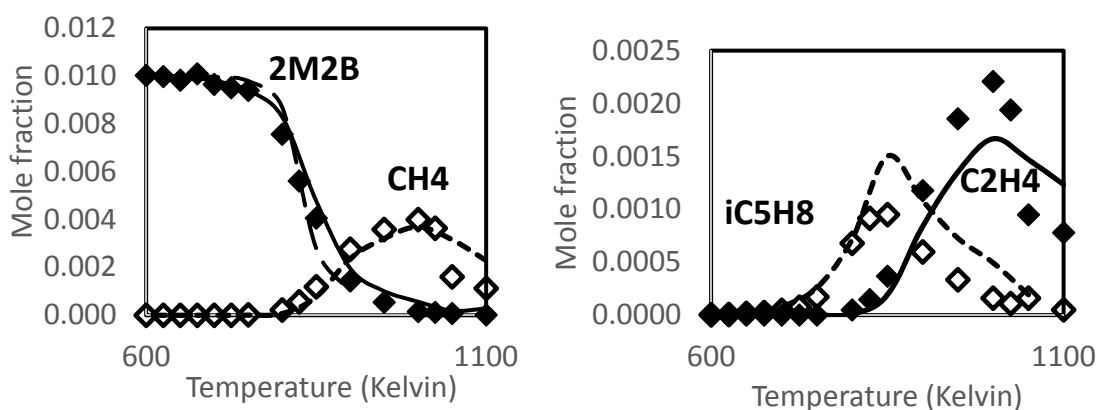
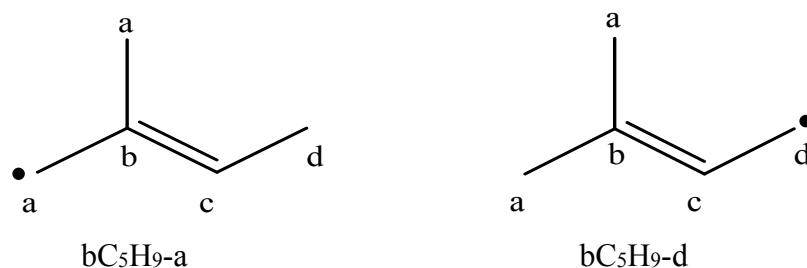


Fig. 2. Comparisons between experimentally measured mole fractions of selected chemical species (symbols) and computed values (lines). Filled symbols and solid lines show results for fuel 2M2B and ethene, open symbols and dashed lines show methane and isoprene (iC₅H₈).

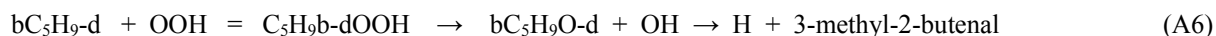
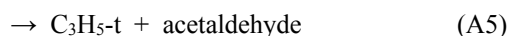
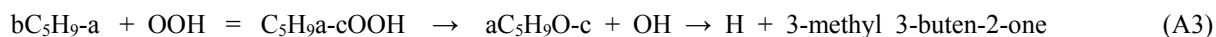
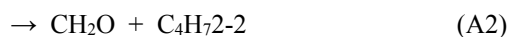
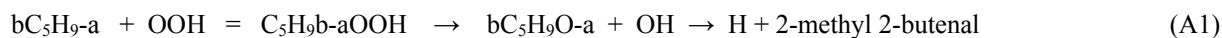
There are two important features of allylic bonds and allylic sites in a fuel molecule. First, allylic C-H bonds are relatively very weak, with bond energies of about 88.5 kcal/mol, while primary, secondary, and tertiary C-H bonds are about 101, 98, and 96 kcal/mol, respectively, and vinylic C-H bonds are about 110 kcal/mol. Therefore, virtually all H atom abstraction from 2M2B occurs at the allylic sites. Abstraction of H atoms from allylic sites in 2M2B produces two possible allylic pentenyl radicals,

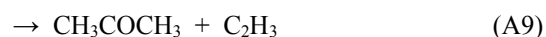
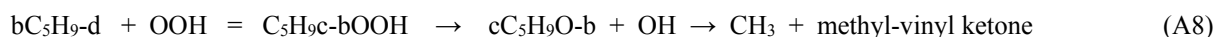
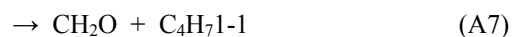


where the H atom has been removed from the ‘a’ site (left) and from the ‘d’ site (right). In addition, as noted previously [4], bonds at allylic sites between C and O₂ are also much weaker than corresponding C – O₂ bonds in alkyl radicals, which suppresses initiation of familiar alkylperoxy radical isomerization reaction sequences that lead to cool flames and NTC behavior that accelerate oxidation in alkane fuels.

The second important feature of allylic radicals is that these radicals are unusually stable against thermal decomposition. Their thermal decomposition reaction activation energies are high, about 50 kcal/mol, especially high when compared with rates of thermal decomposition of alkyl or other non-allylic radicals ($E_a \simeq 35$ kcal/mol). Thus, while alkyl radicals decompose to smaller products quite readily when they are produced from alkane fuels, structurally similar allylic radicals do not decompose until they reach temperatures significantly higher than those where alkyl radicals are consumed by thermal decomposition.

Instead of decomposing or adding to molecular oxygen at intermediate temperatures (i.e., 600-800K), allylic radicals are instead consumed primarily via radical addition reactions, specially addition by OH, HO₂ and H, to produce larger radical species that eventually decompose, but they do this decomposition at temperatures higher than the temperatures at which alkyl radicals in saturated hydrocarbon fuels decompose. The major reactions of the allylic radicals at these intermediate temperatures can be summarized:





Each of these reaction pathways leads to a unique set of products, and each set of product species then is consumed on the way to final products including H_2 , H_2O , CO and CO_2 . The model accurately reproduces each of these intermediate and final products [5], lending confidence in the capabilities of the chemical kinetic model.

The key to these allylic radical reaction pathways is that the products of the allylic pentenyl + HO_2 reactions are metastable hydroperoxide species $\text{C}_5\text{H}_9\text{OOH}$ which, like the ketohydroperoxide species produced by saturated hydrocarbon fuels [8], will not decompose until the temperature is reached that can break the O – O bond, at about 900K. Similarly, because of the high activation energies of the allylic radical decomposition reactions, the relatively large number of allylic radicals that are produced by H atom abstraction from the olefin fuel cannot decompose rapidly until the temperatures reach about 900K, another contribution to later ignition of the olefin fuel. The difference between alkane fuels and fuels with allylic sites is that alkyl radicals decompose at temperatures substantially lower than allylic radicals. This picture can be visualized in Fig. 3, showing that the final consumption of the fuel occurs at about 900K in this stirred reactor simulation, where the allylic radicals, as well as the hydrogen peroxide, begins to decompose rapidly.

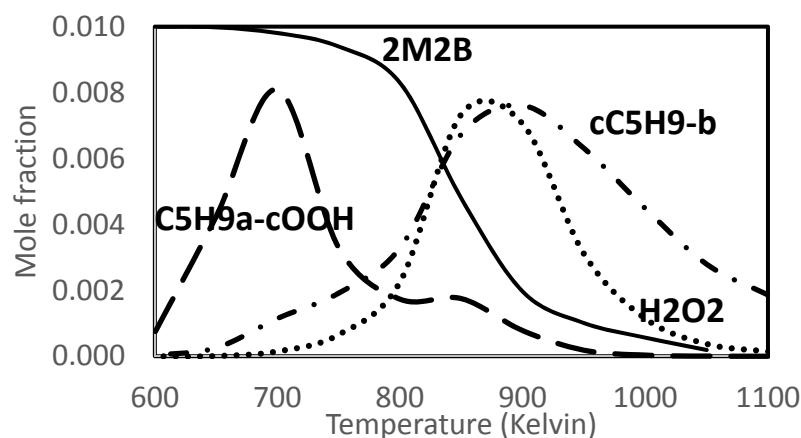


Fig. 3. Stirred reactor simulations of 2M2B oxidation [5], showing mole fractions of fuel and intermediate species, producing rapid reaction or ignition at about 900K.

3. Octane Sensitivity

Perhaps the most familiar tests by which the reactivity of different fuels can be compared are measurements of the Research Octane Number (RON) and Motor Octane Number (MON), and the Octane Sensitivity (OS) is defined as the difference $\text{OS} = \text{RON} - \text{MON}$. While most alkane fuels, including the Primary Reference Fuels (PRF) *n*-heptane and *iso*-octane, but also including many other alkanes, the values for RON and MON are very similar, so for these alkane fuels, the

Octane Sensitivity is close to zero. However, for many olefin fuels, where there is a C=C double bond in the fuel molecule, the MON can be significantly lower than the RON. For example, 2M2B has RON = 97.3 and MON = 84.7 for an Octane Sensitivity of 12.6. For 2M1B, RON is greater than 100 and MON = 81.9 and Octane Sensitivity is greater than 18, and for 3-hexene, RON = 94.0 and MON = 80.1 for Octane Sensitivity is 13.9. Some authors have proposed that Octane Sensitivity can be a very important fuel property [9], particularly for next-generation engines which operate under significant amounts of boosting.

Using our kinetic model, we have taken a careful look at the implications of these octane numbers and how fuels with low sensitivity react differently from those with significant sensitivity. To do this, we must understand how the octane tests operate and what they actually measure. In both the RON and MON tests, test fuel/air mixtures are burned in a special spark-ignition (SI) engine in which the engine cycle is varied in different ways until the test fuel begins to experience engine knock, and then repeating the same tests with PRF mixtures until the two fuels knock at the same times. In general terms, the MON engine test is carried out at 900 rpm while the RON test is done at 600 rpm, and the initial temperature in the MON is higher than that in the RON test (415K vs. 367K). We will return to these distinctions below.

It is essential to understand that, if two fuels are burned in the same octane test conditions, a higher octane number fuel will ignite later than a lower octane number fuel. In addition, every fuel/air mixture in any of the octane tests is subjected to a steadily increasing pressure and temperature due to steady compression from piston motion and also due to secondary compression due to fuel reaction in the flame that is initiated by the spark-ignition. Ideally, we hope to be able to take a Lagrangean sample of fuel and air, and then impose the same pressure/time and temperature/time history on that sample as that resulting from the actual octane number tests. We are developing that capability, but we can learn a great deal from a slightly less accurate series of model computations, as long as we use a kinetic model that has been thoroughly validated over the reaction temperatures and pressures as the real octane tests. Instead, we have used a series of stirred reactor simulations to compute a measure of fuel reactivity as a function of temperature.

4. Simulations

We have used detailed kinetic reaction mechanisms to compute reactivity for a number of fuels and fuel mixtures, using the present 2M2B mechanism for the smaller fuels, and a larger fuel kinetic mechanism for PRF and TRF fuel mixtures [10]. Simulations were carried out for stoichiometric fuel/air mixtures at 10 bar and 40 bar pressures, with reactor residence times of 0.1s for the 10 bar simulations and 0.05s for the 40 bar simulations. In Fig. 4 the results at 10 bar are shown for fuels 2M2B, iso-octane (i.e., PRF100, RON=MON=100), and for RON90 (90% iso-octane, 10% n-heptane). The simulated curves for PRF90 and PRF100 show very similar behavior, with initial reactivity beginning at about 600K, a small but fairly prominent NTC behavior between 700 and 800K, and overall reactivity then rising rapidly above 800K. Similar simulations (not shown) for PRF97 show results in between the curves for PRF90 and PRF100. For 2M2B, reactivity does not begin until about 680K and rises rapidly to a plateau by about 700K and then increasing slowly as temperature increases above 800K. Recall that 2M2B has a RON = 97.3 and MON = 84.7.

Sub Topic: Chemical Kinetics

The initial puzzle was that both 2M2B and, by inference, PRF97 have the same value of RON but show very different amount of low temperature reactivity. Yet because both fuels have the same value of RON, we know that both reach ignition at the same time in the RON test process.

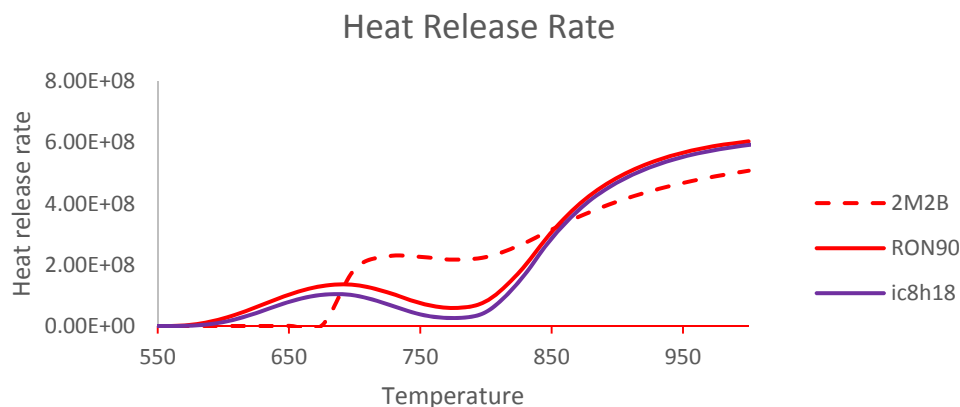


Fig. 4. Reactivity plots for PRF90, PRF100 and 2M2B for stoichiometric fuel/air mixtures at 10 bar pressure, under stirred reactor conditions with a residence time of 0.1s

Therefore, since the RON97 fuel has much more reactivity in the cool flame regions, it proceeds further towards ignition initially. However, the 2M2B must have a greater reactivity at temperatures above the NTC region, if they are to ignite at the same elapsed time. An even greater initial puzzle was that 2M2B has a considerably lower value of MON (i.e. 84.7) than PRF97 (by definition, MON=97). Therefore, the overall reactivity of the 2M2B is greater than that of the PRF mixtures in the MON testing process.

The solutions to these puzzles is clearly that, as shown in Fig. 4, the temperature-dependent reactivities of these two fuels are quite different. In addition, the RON and MON tests are sufficiently different and test different reaction characteristics of each fuel. As already noted, the MON test begins at a higher temperature than the RON test, and since the MON test uses a higher engine speed than the RON test (900 vs. 600 rpm), the fuel/air mixtures traverse the lowest range of temperatures more rapidly in the MON test. In the RON test, the amount of reactivity is initially much greater for RON97 at the lowest temperatures than for 2M2B, but the subsequently greater reactivity of the 2M2B above 700K for the conditions used in Fig. 4 compensate for the differences in the lowest temperature reactivity, so the two fuels ignite at the same time.

In the MON test, the lowest temperature contributions to fuel/air reactivity are minimized overall, partly because the MON test begins at a higher temperature than in the RON test and, due to the higher engine speed, the fuel/air test mixture is in the low temperature region for a considerably smaller time, than in the RON test.

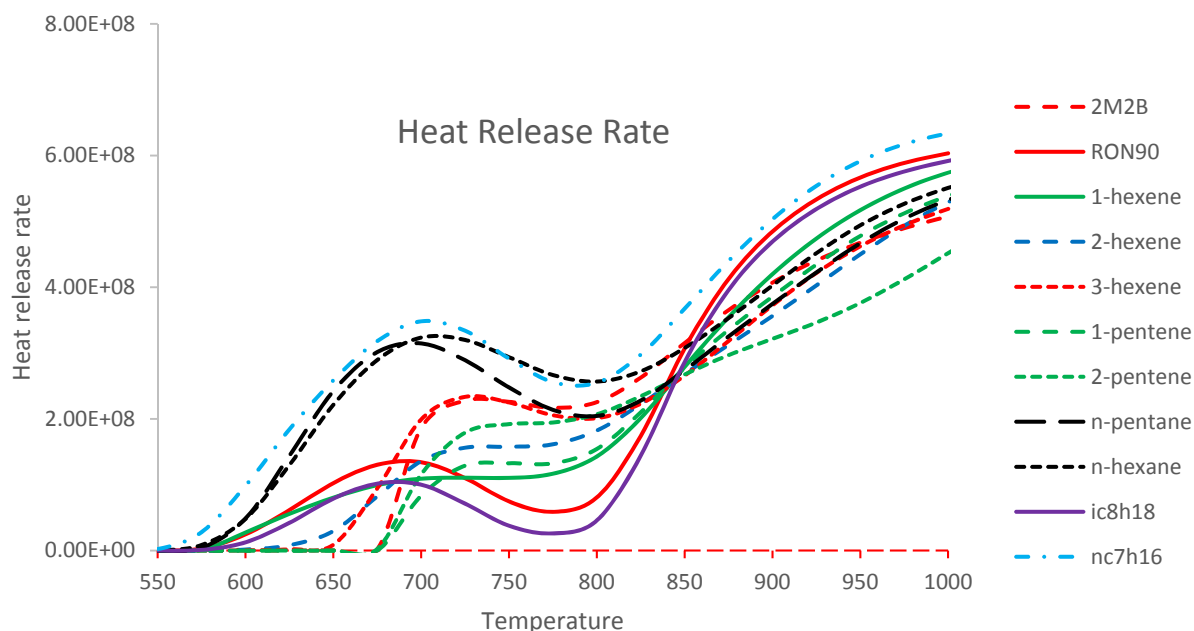


Fig. 5. Reactivity simulations for a wide variety of fuel/air mixtures, same conditions as in Fig. 4.

In Figure 5, similar reactivity simulations are summarized for a range of fuels with both high and low RON and MON values. The high ON range represented for RON90 and RON100 are the same as in Fig. 4, showing considerable low T reactivity between 600-750K, a period of low reactivity and then a rapid rise in reactivity above 800K. The low ON fuels are the n -alkanes, n -pentane, n -hexane and n -heptane, all of which show large reactivities in the low temperature range, significant NTC behavior over the same temperature range as for the RON90 and 100 fuels, and high reactivity at high temperatures. All of these fuels begin to react at about 550-600K, due to the RO_2 initiations of low temperature reactivity. The hexenes are the next family of fuels to react, with 2-hexene and 3-hexene, which have very similar values of $RON \approx 93$ and $MON \approx 80.5$, beginning to react at about 650K and following a pattern similar to 2M2B. An interesting contrast is 1-hexene, which has been studied previously [11,12] and has shown to exhibit some features common to n -alkanes and some features common to olefins, as shown by its initial reactivity beginning at the same lowest temperatures observed here for the n -alkanes.

The final group of fuels are 1-pentene, 2-pentene and 2M2B, for which reactivity does not begin until 700K and exhibits no evident lowest temperature reactivity, consistent with our recent study of 2M2B [5].

5. Discussion and Conclusion

The present work has emphasized that allylic bonds introduced when a hydrocarbon fuel has at least one $C=C$ bond tend to reduce, and in some cases, completely eliminate the low temperature peroxy radical isomerization kinetics that lead to cool flame phenomena. Although the abstraction of H atoms from the fuel is more rapid from allylic sites in the fuel, those allylic radicals cannot

subsequently add rapidly to O₂ and they cannot thermally decompose at the temperatures characteristic of alkyl radical decomposition in alkane fuels. At first glance, this suggests that olefins ought perhaps to have uniformly higher RON and MON values than similar alkane fuels since they initially react so much more slowly than alkane fuels. However, once the temperatures increase sufficiently so that the allylic radicals decomposition can take place rapidly, the high rate of H atom abstraction from allylic sites appears to overcome all of the low temperature reaction-retarding kinetic obstacles to ignition and generally accelerate the overall rate of reaction and ignition. The delay in decomposition of the main radical species, allylic radicals in the present cases, has a minimal effect in the MON test, but the lower temperatures in the RON test slow the overall reaction for the unsaturated fuels and give the alkane fuels enough additional reactivity to compensate for those delays.

6. Acknowledgements

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7. References

- [1] C.K. Westbrook, W.J. Pitz, O. Herbinet, H.J. Curran, E.J. Silke, *Combust. Flame* 156 (2009) 181-199.
- [2] S.M. Sarathy, C.K. Westbrook, M. Mehl, W.J. Pitz, C. Togbe, P. Dagaut, H. Wang, M.A. Oehlschlaeger, U. Niemann, K. Seshadri, P.S. Veloo, F.N. Egolfopoulos, T. Lu, *Combust. Flame* 158 (2011) 2338-2357.
- [3] M.A. Oehlschlaeger, J. Steinberg, C. K. Westbrook, W.J. Pitz, *Combust. Flame* 156 (2009) 2165-2172.
- [4] C.K. Westbrook, C.V. Naik, O. Herbinet, W.J. Pitz, M. Mehl, S.M. Sarathy, H.J. Curran, *Combust. Flame* 158 (2011) 742-755.
- [5] C.K. Westbrook, W.J. Pitz, M. Mehl, P.-A. Glaude, O. Herbinet, S. Bax, F. Battin-Leclerc, O. Mathieu, E.L. Petersen, J. Bugler, H.J. Curran, submitted for publication, 2015.
- [6] W.G. Lovell, *Indust. Engin. Chem.* 40 (1948) 2388-2438.

[7] W.R. Leppard, W. R.; *A Comparison of Olefin and Paraffin Autoignition Chemistries: A Motored Engine Study*, SAE Paper 892081, SAE: Warrendale, PA, 1989.

[8] H.J. Curran, P. Gaffuri, W.J. Pitz, C.K. Westbrook, Combust. Flame 114 (1998) 149-177.

[9] G. Kalghatgi, H. Babiker, J. Badra, *A Simple Method to Predict Knock Using Toluene, n-Heptane and iso-Octane Blends (TPRF) as Gasoline Surrogates*, SAE Paper 2015-01-0757, SAE: Warrendale, PA, 2015. G. Kalghatgi, R. Head, J. Chang, Y. Viollet, H. Babiker, A. Amer, "An Alternative Method

[10] M. Mehl, W.J. Pitz, C.K. Westbrook, H.J. Curran, H.J., Proc. Combust. Inst. 33, (2011) 193-200.

[11] M. Mehl, G. Vanhove, W.J. Pitz, E. Ranzi, Combust. Flame 155 (2008) 756-772.

[12] R. Bounaceur, V. Warth, B. Sirjean, P.-A. Glaude, R. Fournet, F. Battin-Leclerc, F.; Proc. Combust. Inst. 32 (2009) 387-394.